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Title: PIEZOELECTRIC PROPERTIES OF SOME TITANATES AND ZIRCONATES

OF BIVALENT METALS THAT POSSESS A PEROVSKITE-TYPE STRUCTURE
(USSR) by G. A. Smolenskiy

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PIEZOELECTRIC PROPERTIES OF SOME TITANATES

AND ZIRCONATES OF BIVALENT METALS THAT POSSESS

A PEROVSKITE-TYPE STRUCTURE

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Author Abstract: The dielectric permeability of some titanates and zirconates of bivalent metals that possess the structure of perovskite was investigated. It was found that cadmium titanate, lead titanate and lead zirconate and also solid solutions $(Ca, Pb)TiO_3$ and $(Sr, Pb)TiO_3$ are piezoelectric. It was proved that the Curie temperature of these piezoelectrics is most influenced by the degree of covalence of the lattice bond and by the dimensions of the oxygen octahedron, which contains a titanium ion. It was proved that piezoelectrics of this type have a tetragonal lattice below the Curie point.

Investigations by Wul and Goldman showed that barium titanate is piezoelectric. Recently many works have been devoted to the study of the properties of barium titanate and its compounds. In particular it was found that solid solutions of barium titanate with strontium titanate and lead titanate are also piezoelectric.

The Curie temperature of solid solutions $(Ba, Sr)TiO_3$ decreases with increase of the amount of strontium titanate. In solid solutions $(Ba, Pb)TiO_3$ the opposite effect takes place; namely, the Curie temperature increases with increase of lead titanate.

1. STATEMENT OF THE PROBLEM

The polycrystalline barium titanate has a cubic structure of the perovskite type, and its lattice is distorted somewhat in the piezoelectric state.

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A similar structure is shared by a series of compounds ABO_3, where A means bivalent metals like Ca, Sr, Ba, Cd, Pb and B means quadrivalent metals like Ti, Zr, Sn, Hf, Th, and Ce.

Obviously the piezoelectric properties of a substance depend closely on its structure. For instance barium titanate crystals were obtained with hexagonal and monoclinic syngony and these had no piezoelectric properties. Hence it is inferred that spontaneous polarization appears in barium titanate only in the case of a peroskite structure. Consequently we should expect piezoelectric properties in substances of similar strufture.

The assumption that strontium titanate is also piezoelectric has already been expressed by Rushman and Streivens. But until recently sufficiently convincing proofs of piezoelectric properties in strontium titanate were not yet published. All known ceramic substances that show piezoelectric properties possess barium titanate in their composition.

Barium titanate is somewhat different from other titanates and zirconates. In its lattice the distance between titanium and oxygen ions is greater than the sum of their radii, according to Goldshmit, with the resulting possibility of transition of the titanium ion inside the octahedron. (Figure 1).

We assume, despite this property of barium titanate, that not only the latter substance but also a whole series of ABO_3 compounds containing titanium and zirconium ions, and possibly also other quadrivalent cations having a type structure perovskite, possess piezoelectric properties.

With this assumption, we studied a number of titanates and zirconates of bivalent metals and also some of their solid solutions.

Preliminary investigations of the electric properties of lead titanate and lead zirconate showed that these compounds probably are piezoelectric with a Curie point in the region of high temperatures. The fact that at room temperature these substances, like barium titanate, had a tetragonal lattice confirmed our assumption. According to preliminary data the lattice of lead zirconate becomes cubic at temperatures over 300°C.

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It is possible to study lead titanate's dielectric permeability at temperatures only up to 500°C. Lead titanate's conductivity at high temperatures rises so strongly that the equipment available to us is insufficient to obtain the readings.

Therefore we studied the properties of the solid solutions $(Ca, Pb)TiO_3$ and $(Sr,Pb)TiO_3$. We based our investigations on the assumption that strontium titanate and calcium titanate's piezoelectricity occurs only for low Curie temperatures. With a certain concentration of titanates we should get compounds with a Curie point that is within an easily measurable range.

2. PREPARATION OF SAMPLES

The first samples prepared contained titanium dioxide, zirconium dioxide, chemically-pure barium carbonate, strontium carbonate, calcium carbonate, and lead dioxide. The chemical analysis of titanium dioxide and zirconium dioxide is represented in Table 1 (see appendix).

Titanates and zirconates, as well as their solid solutions of the initial constitutents, form at high temperatures as a result of the reaction between the solid phases. It is known that, for better reaction processes in the solid phases, the components must be finely dispersed. The initial materials were finely pulverized in a metallic mortar. The grain size did not exceed $3 - 5 \mu$. Disc-shape samples 10 to 30 mm in diameter were prepared under pressures of 1000 kg/cm^2.

In order to increase plasticity, an aqueous dextrin solution (5% by weight) was added to the initial mixtures. The baking was done in Silit and platinum furnaces at temperatures 1000 to 1450°C. As a rule we did not succeed in getting fully baked samples, because lead titanate and lead zirconate are chemically unstable at high temperatures. Samples of lead zirconate and samples with strong lead titanate content were baked at temperatures of 1000 - 1180°C with long exposure at high temperatures.

Some samples were preliminary baked at 100 - 150°C below the final temperature; thereafter they were carefully pulverized, pressed and baked again. Calcined samples were less porous.

The electrodes were processed by burning in silver at 800 - 850°C.

3. RESULTS OF EXPERIMENTS

First we investigated compounds in which lead titanate gradually changed into calcium titanate. Here we cannot ascertain whether lead and calcium titanates form a continuous series of solid solutions.

Lead titanate samples were baked at temperatures of 1050 - 1100°C with rather long exposures, in some cases lasting 20 to 24 hrs. With increasing calcium titanate content the baking period was increased. Pure calcium titanate was baked for an hour at 1430°C. Samples with large lead titanate content had porosity reaching 25%. Further increase of the baking temperature was impossible, because at temperatures above 1100°C lead titanate starts to decompose intensively.

The real dielectric permeability of the substance was determined, taking the porosity into consideration, by V. I. Odolevskiy's formula:

$$\frac{\varepsilon - \varepsilon_{meas}}{\varepsilon - 2\varepsilon_{meas}} (1 - x) + \frac{1 - \varepsilon_{meas}}{1 + 2\varepsilon_{meas}} x = 0 . \tag{1}$$

Where epsilon ε is the real dielectric permeability; ε_{meas} is the apparent dielectric permeability, that is, ε obtained from measurements of the samples' capacity; x is relative porosity (in fractions).

This formula, which was obtained for symmetrical systems, cannot be accurately applied in our case and probably gives somewhat lowered values of the real permeability.

In applying Lichtenecker's well-known relation, we see that the real dielectric permeability has a much higher value than that obtained from formula (1). Odolevskiy showed that the Lichtenecker's logarithmic formula is in agreement with tests in the case of small discrepancies where permeability is for the components of a heterogeneous system.

Table 2 shows values obtained for ε-samples of the titanate system $CaTiO_3$ - $PbTiO_3$ baked at various temperatures, their porosity and their real dielectric permeability.

The ratio of real dielectric permeability of calcium lead titanates and molar concentration PbTiO$_3$ is represented graphically in Figure 2. The dielectric permeability was measured for field strengths 1 to 2 V/mm, temperature $20 \pm 1^\circ$C and frequency 10^6 cycles with a tolerance of $\pm 2 - 3\%$.

The dependence of the characteristic ratio on piesoelectrics upon permeability (or capacity) and the dielectric-loss tangent upon temperature was observed in a number of compounds (Figures 3 and 4).

The relation between temperature and dielectric permeability of lead titanate is represented on Figure 5.

Similar measurements were made for some solid solutions (Sr,Pb)TiO$_3$. Strontium titanate was baked at a higher temperature than calcium titanate because of lead titanate's instability at high temperatures. As a rule we did not succeed in completely baking the samples. The porosity of samples measured reached 35% sometimes even 40%.

The relation between temperature and dielectric permeability of two solid solutions (Sr,Pb)TiO$_3$ is shown on Figure 6.

Usually the capacity of samples was measured at a frequency of 10^6 cycles and electric field strength of 1 to 2 V/mm. For one-component samples the relation between capacity and temperature was measured at two frequencies: 800 and 10^6 cycles (Figure 7).

Table 3 shows experimental values of ε-samples of solid solutions (Sr,Pb)TiO$_3$, their porosity and real dielectric permeability. It should be noticed that the determination of porosity was considerably inaccurate because of the small sample sizes.

The dependence, upon molar concentration of PbTiO$_3$, of the dielectric permeability of these solid solutions is shown graphically in Figure 8.

Zirconates of bivalent metals were less completely studied. Such studies will be done later.

Test results of the electric properties of lead zirconate are shown on Figure 9.

Lead zirconate and lead titanate are unstable at high temperatures. Therefore measurements were conducted with porous samples. The samples were baked for 24 hrs at $1000^\circ C$.

Tests with a cathode oscillograph proved that the solid solutions $(Ca,Pb)TiO_3$ and $(Sr,Pb)TiO_3$ possess dielectric hysteresis within a certain temperature range.

4. DISCUSSION OF EXPERIMENTAL DATA

Test results make us believe that lead zirconate and the solid solutions $(Ca,Pb)TiO_3$ and $(Sr, Pb)TiO_3$ (for certain concentrations of basic titanates) are piezoelectric. All the experimental data obtained convince us of this.

The temperature dependence of dielectric permeability and losses of each compound investigated are typical of piezoelectrics. It is true that the permeability of the substances studied has a lower value than that of barium titanate. It should be kept in mind, however, that the test results depend strongly on the baking process. Even at comparatively low baking temperatures $(1000 - 1150^\circ C)$ lead titanate and lead zirconate start to decompose and their lattices become somewhat spoiled.

Within a certain temperature range the titanates investigated show a dependence of dielectric permeability upon field strength and dielectric hysteresis.

It is known that the location of maximum permeability in the curve of ε does not depend on temperature. It occurs also in our case.

The dielectric permeability of the investigated solid solutions and of barium and strontium titanates varies in a similar way, depending on the concentration of the initial components.

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Other investigated titanates and zirconates of bivalent metals, except cadmium titanate, did not show piezoelectric properties until ~180°C. As we recently succeeded in proving, cadmium titanate is piezoelectric with a Curie point somewhat below - 180°C.

Thus the results obtained confirmed the earlier above-expressed assumptions. Piezoelectric properties do not pertain exclusively to barium titanate, but are found also in other titanates and zirconates of bivalent metals. This follows logically from our known data on the properties of $BaTiO_3$.

Let us start with barium titanate. The latest X-ray researches show that the titanium ion is not located in the center of the oxygen octahedron. This phenomenon permitted Mason and Matthias to create a theoretical model in order to explain the piezoelectric state of $BaTiO_3$.

According to recent notions, the bond of the titanium ion is partially convalent with the oxygen ions. Because of this covalent character of the bond the titanium ion shifts to one of the six adjacent oxygen ions a distance equal to $\sim$ 0.1 A from the center of the octahedron. Obviously the oxygen ion shifts too towards the titanium ion. We should assume that the oxygen ion shifts a much lesser distance than the titanium ion.

Hence the oxygen octahedron has six positions in which the potential energy of the titanium ion is a minimum. Above the Curie point, because of the effect of thermal motion, it is equally likely to find the titanium ion in any one of these positions.

The asymmetrical position of titanium and oxygen ions in an elementary cell of $BaTiO_3$ produces a dipole moment, whose value may be determined from the following expression

$$\mu = e_1 l_1 + e_2 l_2 \tag{2}$$

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where e_1 is the charge of a titanium ion, equal to $4e$ (e is the charge of an electron) l_1 is the value of the titanium ion displacement with respect to the center of the $BaTiO_3$ octahedron and equals 0.1Å; e_2 is the charge of the oxygen ion and equals $2e$; l_2 is the displacement of the oxygen ion, and is $\ll l_1$.

Below the Curie point the kinetic energy of thermal motion is not sufficient to ensure the possibility of one of the six positions. The titanium ions straighten out along one of the directions within the limits of the domain, while the $BaTiO_3$ crystal passes from cubic to tetragonal, because the axis along which the titanium ions are alined/becomes longer than the other two.

On these assumptions Mason and Matthias determined the Curie temperature

$$\theta = \frac{\beta N \mu^2}{3K} \left[1 + \frac{\beta(\mathcal{E}_0 - 1)}{4\pi} \right] \tag{3}$$

where bota β is the Lorentz coefficient; N is the number of dipoles in a cm^3; μ is the dipole moment; $\mathcal{E}_0$ is the dielectric permeability due to the electron and ion polarization; k is the Bolzmann constant.

These discussions can be expanded to other piezoelectrics of the type ABO_3 with a perovskite-type structure.

The Curie temperature of such piezoelectrics will first be determined by the value of the dipole moment produced by the asymmetrical position of quadrivalent cations; while the greater the covalent bond character in the lattice and the greater the size of the oxygen octahedron for a given radius of the quadrivalent cation, the greater the dipole moment. Assuming further that the oxygen ion moves towards the quadrivalent cation a much shorter distance than the latter, we will consider only the displacement of the quadrivalent cation.

The size of the oxygen octahedron is much effected by the size of the bivalent cation. The greater the bivalent cation for a given radius of the quadrivalent one, the greater the size of the oxygen octahedron.

The displacement of the titanium ion in a barium titanate lattice, with respect to the center of the octahedron, is easy to imagine, because the distance between the titanium and oxygen ions is greater than the sum of their radii according to Goldshmit.

According to Goldshmit, however, the radii cannot be a criterion in our case. Probably the quadrivalent cation can be located asymmetrically within the oxygen octahedron even when the sum of ion radii according to Goldshmit is bigger than the distance between them. In this case a kind of mutual interpenetration of electron shells of ions will take place. It may be observed particularly in barium titanate. As mentioned, the titanium ion is displaced with respect to the octahedron center by about 0.1Å.

The difference of the distances of the titanium - oxygen ion centers and the sum of their radii along the c axis equals only 0.053Å. This fact explains the appearance of piezoelectric properties of some other ABO_3 compounds.

Depending upon the electron structure of exterior shells of bivalent cations definitely affecting the covalent character of lattice bonds, we should distinguish three groups of titanates: 1) alkali-earth metals, 2) cadmium, 3) lead.

The atoms of alkali-earth metals Ca Sr, and Ba after emission of bivalent electrons are similar to the atoms of inert gases. The bivalent cadmium ion has a different electron structure. The covalent bond in cadmium oxides is stronger than in similar metal compounds of the left sub-group II in the periodic table. The lead atom, after emission of bivalent electrons, retains two electrons in the exterior shell. Megaw remarks that the lead ion cannot be considered as an incomplete sphere and probably forms covalent compounds.

Let us analyse the titanates of bivalent metals possessing perovskite structure with respect to previous statements.

The Curie temperature of these titanates is represented in Table 4.

The Curie temperature of alkali-earth titanates, as it should be expected from previous theoretical assumptions, drops steeply with decreasing radius of the bivalent cation and therefore with the decreasing oxygen octahedron.

The Curie point of cadmium titanate is within the region of temperatures higher than the Curie point of strontium titanates, despite the fact that a strontium ion is bigger than a cadmium ion. The Curie temperature of lead titanate is much higher than the Curie temperature of barium titanate, despite the fact that the lead ion is somewhat smaller than the barium ion.

In cadmium titanate and lead titanate the real titanium - oxygen bond character is probably more pronounced than in alkali-earth titanates. This statement is reflected in the fact that spontaneous polarization disappears at relatively higher temperatures.

On the basis of previous statements we may infer that the Curie temperature of $AZrO_3$ compounds should be lower that of corresponding titanates. The zirconium ion is bigger than the titanium ion and the covalent bond character of oxygen with zirconium is probably less pronounced than the bond of oxygen and titanium. In effect, the Curie temperature of lead zirconate does not exceed $279^\circ C$, while that of lead titanate is over $500^\circ C$. It follows therefore that if barium zirconate has piezoelectric properties they should occur only at very low temperatures.

The following general case should be mentioned: the compounds ABO_3 have a tetragonal lattice within their piezoelectric range. According to Megaw's data, only three compounds ABO_3 have a tetragonal lattice at room temperature, these being $BaTiO_3$, $PbTiO_3$, and $PbZrO_3$; as proved by Wul ($BaTiO_3$) and by us ($PbTiO_3$ and $PbZrO_3$) the mentioned substances are piezoelectric within this temperature range.

Table 5 shows the axis ratio $\frac{c}{a}$ for a tetragonal structure of ABO_3 compounds.

Careful X-ray researches prove that during the transition period of barium titanate to the piezoelectric state one axis lengthens, while the two others shorten. This agrees well with the assumption that titanium ions shift from the octahedron center to an adjacent oxygen ion. These discussions hold completely for lead titanate. The fact that the axis ratio $\frac{c}{a}$ is bigger in $PbTiO_3$ than in $BaTiO_3$ entirely confirms our reasoning. Evidently, because of the more pronounced covalent bond character in lead titanate, the titanate ion is more displaced with respect to the octahedron center, which results in an increase of the tetragonal lattice.

Lead zirconate differs from other piezoelectrics $ATiO_3$. Its axis ratio $\frac{c}{a}$ is smaller than unity. This proves that in $PbTiO_3$ during the transitory state to piezoelectricity two axes lengthen and one shortens.

It is very interesting to grow and investigate single lead zirconate crystals.

The author expresses his gratitude to Prof. P. P. Kobenko for his expert opinion in the discussions.

[Note: The tables and figures follow]

Table 1

Name of the Substance	ZrO_2	SiO_2	Fe_2O_3	Al_2O_3	TiO_2	CaO	MgO	NaO	SO_3	P_2O_5	Losses during Annealing
Titanium Dioxide	Not determined	Traces	0.033	Not determined	98.5	Not determined			0.08	0.04	0.72
Zirconium Dioxide	96.68	1.78	0.23	Not Determined				0.40	0.60	–	0.44

Table 2

Concentration in Molar Percents	$CaTiO_3$	100	90	80	70	60	50	40	37.5	35	32.5	30	25	20	10	0
	$PbTiO_3$	0	10	20	30	40	50	60	68.5	65	67.5	70	75	80	90	100
Apparent Dielectric Permeability		141.5	149	143	156.5	287	357	700	693	707	661	602	394	256	162.5	46
Prosity in Ffactions		0.063	0.131	0.193	0.20	0.139	-	0.213	0.263	0.238	0.226	0.123	0.153	0.155	0.176	0.40
True Dielectric Permeability		156.5	185.5	201.5	224	400	-	1030	1144	1100	1000.5	740	512	334	220.5	115

Table 3

Concentration in Molar Percents	$SrTiO_3$	100	90	80	70	60	55	50	47.5	45	42.5	40	30	20	10	0
	$PbTiO_3$	0	10	20	30	40	45	50	52.5	55	57.5	60	70	80	90	100
Apparent Dielectric Permeability		265	120	134	327	603	642	875	374	267	215	261	200	160	78	46
Porosity in Fractions		0.06	0.41	-	0.354	0.235	0.357	0.0166	0.366	0.392	0.360	0.253	0.15	0.147	-	0.40
True Dielectric Permeability		291.5	312	-	699	931	1380	1151	829	648	467	421	258	206	-	115

Table 4

Chemical Formula of the Titanate	Curie Temp.
$CaTiO_3$	-
$SrTiO_3$	15 - 35
$BaTiO_3$	375
$CdTiO_3$	60
$PbTiO_3$	800

Table 5

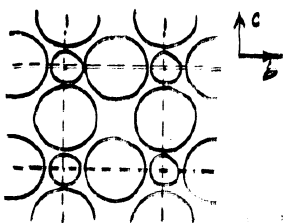| Chemical Formula	τ
$BaTiO_3$	1.0100
$PbTiO_3$	1.0635
$PbZrO_3$	0.988

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Figure 1. Lattice of Barium
Titanate in the (100) Plane
for z = 0.
Oxygen ions are indicated by
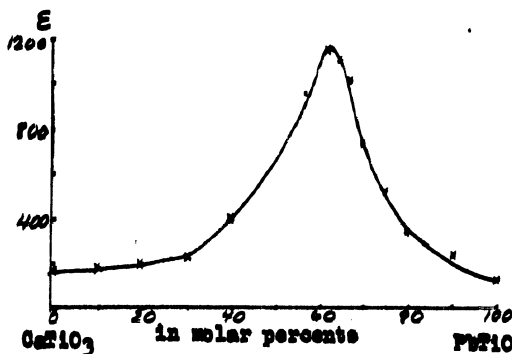the large circles, titanium
ions by the small ones.

Figure 2. The Dependence of the True Dielectric
Permeability of Mutual Solid Solutions (Ca, Pb)TiO$_3$
Upon the Molar Concentration of PbTiO$_3$.
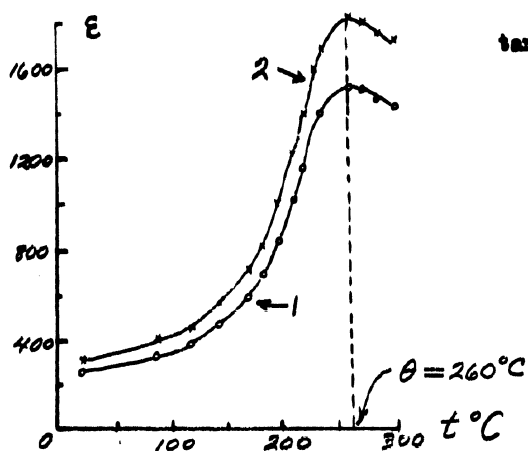
Figure 3. Dependence of the Dielectric
Permeability of the Solid Solution 20:80
(Ca:Pb)TiO$_3$ Upon Temperature.
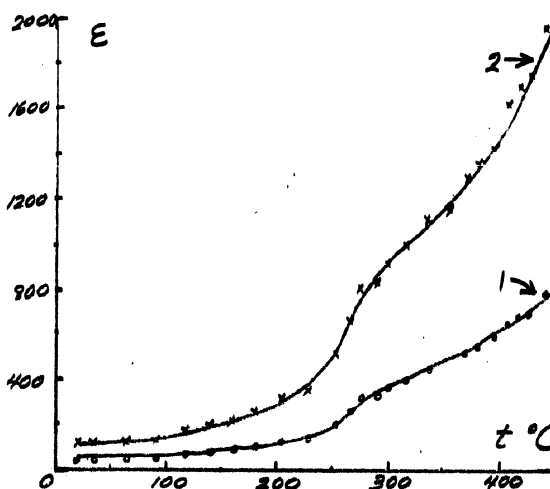1 - apparent dielectric permeability
2 - the true   "   "
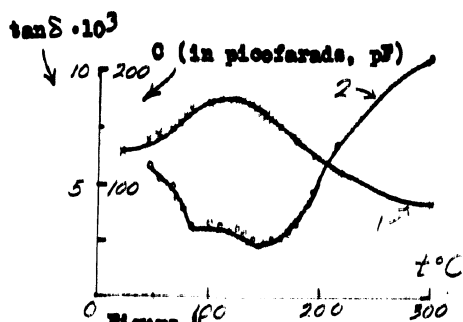
Figure 4.
Dependence of Capacitance C and Dielectric
Loss tan δ of the Sample of Solid Solution
30:70 (Ca:Pb)TiO$_3$ Upon Temperature t.
1 - capacitance, 2 - tan δ .

Figure 5.
The Dependence of the
Dielectric Permeability
of Lead Titanate
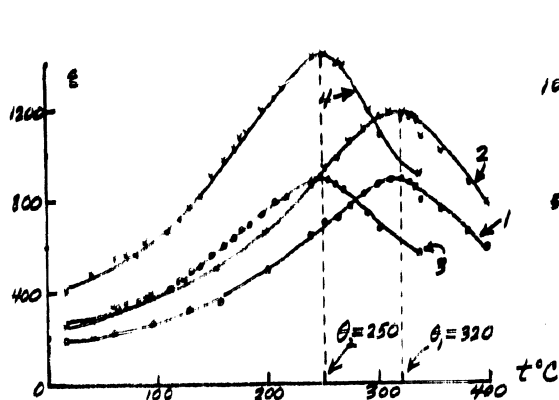Upon Temperature.

1 - apparent
2 - true

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Figure 6. The Temperature Dependence of the
Dielectric Permeability of Two Solid Solutions
(Sr, Pb)TiO₃ .
A. 30:70 (Sr:Pb)TiO₃ . 1- apparent, 2-true.
B. 40:60 (Sr:Pb)TiO₃ . 3- apparent, 4-true.
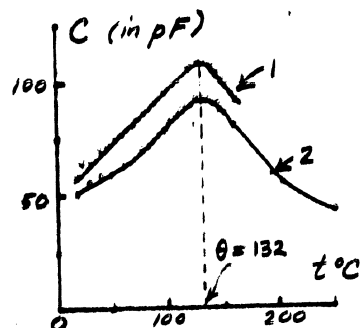
Figure 7. The Temperature
Dependence of the Capacitance
of a Sample Made from a Solid
Solution 50:50 (Sr:Pb)TiO₃ ,
for Various Frequencies, f.
1- f=800 cps, E = 30 v/mm
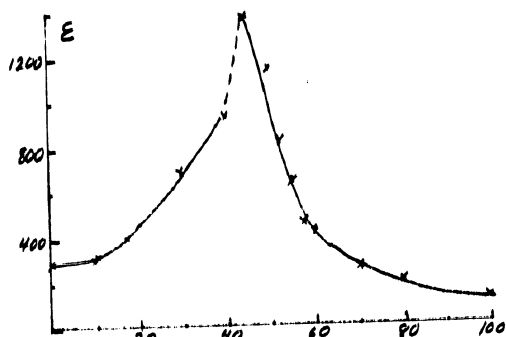2- f=10⁶ cps, E = 1-2 v/mm

SrTiO₃   (in molar percents) PbTiO₃
Figure 8. The Dependence of the True
Dielectric Permeability of Solid
Solutions (Sr, Pb)TiO₃ Upon the
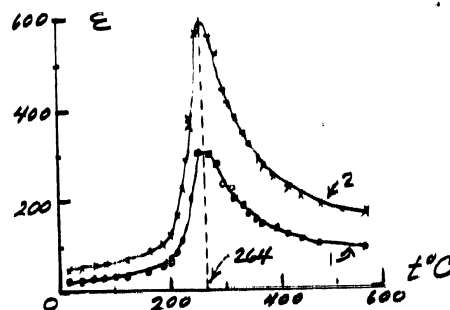Molar Concentration of PbTiO₃ .

Figure 9. The Temperature
Dependence of the Dielectric
Permeability of Lead Zirconate.
1 - apparent , 2 - true.

-15-

-END-